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Chemical analysis of racing fuels using total vaporization and gas chromatography mass spectrometry (GC/MS)

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The National Hot Rod Assocation (NHRA) is the governing body of North American drag racing. As a supervisory agency, NHRA monitors racing fuels for regulatory purposes and quality control. In this paper, total vaporization and mass spectrometry based methods were developed to analyze nitromethane-based and racing gasoline fuels. Total Vaporization Headspace gas chromatography mass spectrometry (TV-HS-GC/MS) was used to quatitate the amount of methanol in nitromethane fuels to verify that the methanol content was at least 10% (v/v). Total vaporization solid phase microextraction gas chromatography mass spectrometry (TV-SPME-GC/MS) was used to qualitatively identify racing gasoline components, which included isopentane, isooctane, toluene, and tetraethyllead.

Introduction

The National Hot Rod Association (NHRA) is the governing body of North American drag racing and is the largest motorsports sanctioning body in the world. Since it was founded in 1951, the responsibility of the NHRA has grown to include over twenty categories of competition, including top fuel, funny car, pro stock, and pro stock motorcycle. In general, race teams are required to purchase approved fuel for their vehicles. Only NHRA sanctioned fuel is allowed and any adulteration is prohibited. Hence, one of the duties of the NHRA is the monitoring of racing fuels before and after all racing events.

One type of fuel that is used in NHRA events is based upon nitromethane. However, the maximum percentage of nitromethane allowed in the blend is 90% by volume, with the remainder consisting of methanol. Due to the oxygen contained within the nitromethane structure, the power output when burned is much higher than that of regular gasoline.

Nitromethane has been previously analyzed using headspace gas chromatography-mass spectrometry (GC-MS) for the purpose of studying canine explosive detection[1]. Quantitation of nitromethane in human blood for the purpose of assessing toxicity was done using solid phase microextraction (SPME) with GC and high resolution mass spectrometry[2]. Another study used activated carbon with gas chromatography flame ionization detection to sample and test nitromethane in air[3].

In addition to nitromethane-based fuels, specialty racing gasolines are used in NHRA events. In general, gasoline contains a complex mixture of aromatic and aliphatic hydrocarbons as well as various additives. For example, lead is added to racing gasoline in the form of tetraethyllead and serves as an octane booster. Gasoline is traditionally analyzed using a variety of methods, such as GC-MS for the detection of added organic solvents[4], near infrared along with multivariate statistical analysis for the classification of gasoline[5], and high performance liquid chromatography with a UV-diode array detector for the measurement of benzene and the total aromatic fraction in gasoline[6].

In this study, nitromethane- and gasoline-based racing fuels have been analyzed using a total vaporization technique. In practice, total vaporization entails placing a known volume of sample inside a sealed vial and heating it until all of the solvent and analytes are forced into the vapor phase. Then, the vapor can be sampled and analytes transferred to a gas chromatograph using either simple headspace extraction or solid-phase microextraction (SPME).

The maximum sample volume that can be vaporized in a given container is dependent on the vapor pressure of the liquid components and the sample temperature, as shown in the following equation,[7]

$$V_s = \left(\frac{\left(10^{A-\frac{B}{T+C}}\right)V}{RT} \right)\left(\frac{M}{\rho}\right) \qquad \text{Equation 1}$$

where A, B, and C are Antoine vapor pressure constants for the solvent (available from various sources, including the NIST Chemistry WebBook), V is the volume of the container (L), R is the ideal gas constant (8.3145×10^{-2} L bar/K mol), T is temperature (K), M is the molar mass of the solvent (g/mol), and ρ is the density of the solvent at the temperature at which it was placed in the vial (e.g., room temperature) (g/mL). An

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important note is that the internal volume of a nominal 20 mL headspace vial is actually larger (e.g., 20.9 mL), which has a small but important effect on the calculated volume[8].

The theory and experimental requirements for coupling total vaporization to solid phase microextraction (TV-SPME) have been discussed previously, as well as the application of TV-SPME to determining nicotine in hair and post-blast explosive residue on bomb fragments[7, 8]. As with any quantitative SPME method, the temperature and time of exposure of the SPME fiber to the sample vapor must be both accurate and precise, hence the use of an auto-sampler is required. A distinct advantage of TV methods is that large sample volumes can be used given the large vapor pressures of most organic solvents. Furthermore, the use of a SPME fiber as a pre-concentration step allows for much greater sensitivity than traditional liquid injection.

Although the data discussed in this paper were generated using a mass spectrometer detector, total vaporization methods should be compatible with any commercially available GC detector. Ultimately, MS was required since all of the fuel samples were treated as true unknowns and MS would be able to identify any prohibited additives.

Materials and methods

Chemicals and reagents

HPLC grade nitromethane (NM, ≥96%) and HPLC grade methanol (MeOH, ≥99.9%) were purchased from Sigma-Aldrich (St. Louis, MO). SPME vials (20 mL) and PTFE lined caps were purchased from Gerstel (Linthicum, MD).

Nitromethane standard preparation

Five calibrants ranging in concentration from 0-20% v/v methanol in nitromethane were prepared. Two test mixes were prepared at 8% and 12% methanol in nitromethane. Twenty microliters of each calibrant were transferred to separate 20mL headspace vials.

Total vaporization (headspace) of nitromethane-based fuels

Samples of nitromethane-based fuels were analysed using total vaporization headspace GC-MS using a Thermo Scientific Triplus autosampler, Trace Ultra GC, and DSQII mass spectrometer. This system was in regular use for separations of complex petroleum products. The conditions, which were set to maximize the chromatographic resolution between methanol and nitromethane whilst avoiding over saturation of the MS detector, are described below.

The sample vials were incubated for 5 minutes at 80°C so that the samples completely vaporized. The headspace syringe was heated to 85°C and injected a sample volume of 1 mL. The sample was split 100:1 in the GC inlet. Hydrogen was the carrier gas, held at 1 mL/min. The inlet temperature was 220°C and the oven was held at 35°C for 4.5 min. The column used was a Zebron ZB-5MS with dimensions of 60 m x 0.25 mm x 0.25 µm (Phenomenex, Torrance, CA). The transfer line temperature was 280°C and the ion source temperature was 200°C. The mass spectrometer was operated in electron impact mode with no solvent delay, scanning a range of m/z 29-100.

Total vaporization (SPME) of racing gasoline

Samples of racing gasoline were analysed using total vaporization headspace SPME using the same GC/MS system. In this case, the system was configured for "fast GC" to allow for maximum chromatographic resolution in a minimum of time. The conditions, which were set to maximize sample size and sensitivity, are described below.

The racing gasoline samples (VP C-25, VP C-23, Sunoco SR-18) were transferred to 20 mL SPME vials (80 µL). The samples were incubated for 5 min at 100°C and extracted for 20 min at 100°C using a polyethylene glycol (PEG) fiber. The fiber was desorbed in the inlet in splitless mode for 1 min at 240°C, and conditioned for 3 min at 240°C. Helium was the carrier gas at 1.5 mL/min. The oven program began at 40°C and was held for 2.5 min. It was then ramped 10°C/min to 280°C and held for 3 min. The column used was a Zebron ZB-5MS with dimensions of 10 m x 0.18 mm x 0.18 µm. The transfer line and ion source were both 250°C. The mass spectrometer was operated in electron impact mode with no solvent delay, scanning a range of m/z 30-500.

Results and discussion

Nitromethane

The maximum volume of any liquid that can be vaporized at a given temperature can be calculated using Equation 1. The calculated maximum volumes of methanol (the analyte) and nitromethane (the solvent) as a function of temperature are shown in Figure 1.

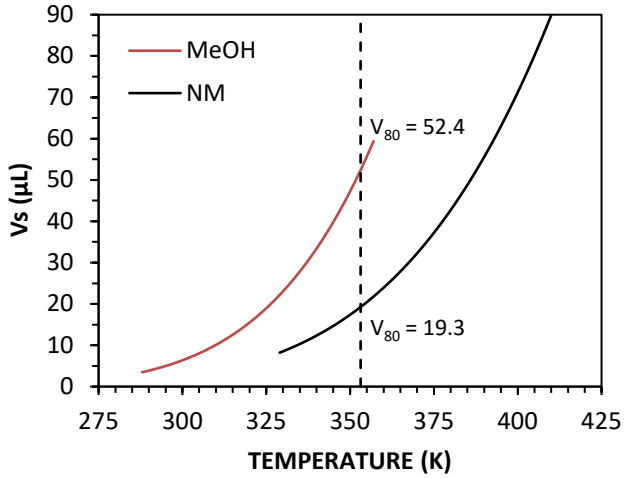


Figure 1: Calculated volume of methanol (MeOH) and nitromethane (NM) that can be vaporized in a nominal 20 mL headspace vial (V = 0.0209 L) as a function of temperature. The dashed line represents an extraction temperature of 80 °C.

In this method, the incubation temperature is 80°C which corresponds to a calculated maximum volume of 52.4 and 19.3 µL of methanol and nitromethane, respectively. The maximum volume of nitromethane was confirmed experimentally by monitoring instrument response while varying the sample volume from 12 – 24 µL. As shown in Figure 2, the instrument response plateaus at 20 µL, in good agreement with the calculated maximum volume.

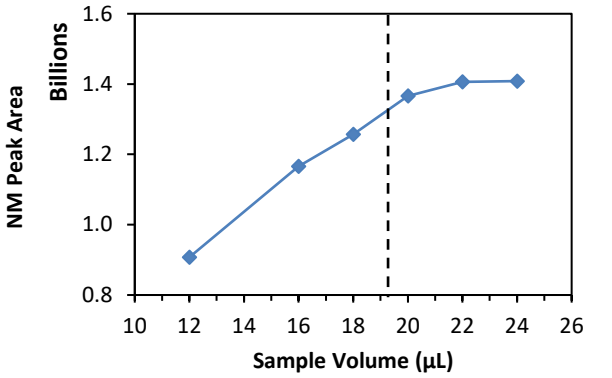


Figure 2: The results of a total vaporization (simple headspace) study showing nitromethane peak area as a function of sample volume. The vertical dashed line represents the maximum sample volume as calculated from Equation (1).

Following the volume study, a calibration curve was made by preparing standards ranging from 0 – 20% methanol in nitromethane (v/v). The linearity was excellent, with a R^2 value of 0.996. The two test mixes of 8% and 12% methanol in nitromethane were determined experimentally to be 8.8% and 13.4% using this method. This corresponds to a relative error of 10% and 12%, respectively. This method was successfully used in the testing of several nitromethane-based racing fuels drawn from vehicle fuel tanks, as shown in Figure 3. In this case Fuel #1 and Fuel #2 were not compliant as they did not contain any detectable methanol. In contrast, fuel #3 was compliant as it contained 13% v/v methanol.

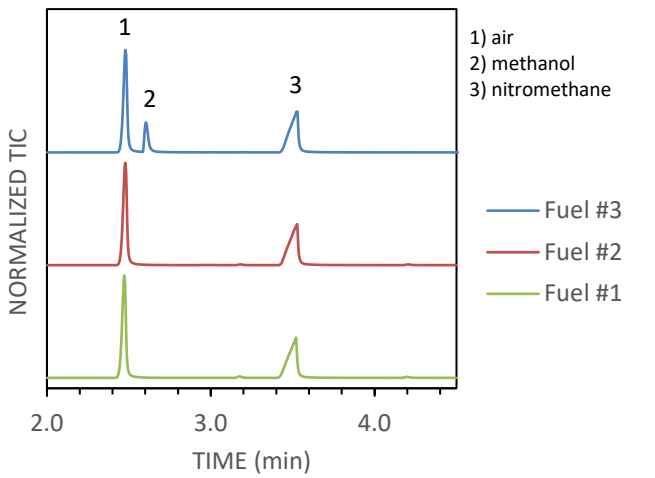


Figure 3: Example chromatograms of nitromethane fuel samples taken from three different vehicles. See materials and methods section for instrument parameters.

Racing gasoline

The major component of the racing fuels tested is isooctane. Using Equation 1, the theoretical maximum volume of isooctane that can be vaporized at 100°C is 109 µL. To be conservative, 80 µL of fuel was used for this analysis. Two racing gasolines from the manufacturer VP Racing (C25 and C23) were analysed. It was determined that C25 contained multiple branched alkanes and aromatic hydrocarbons, including isooctane and butylated hydroxytoluene. In one instance, a fuel sample from a car looked noticeably different than the C25 reference (Figure 4). The car fuel had a mixture of straight and branched hydrocarbons with boiling points between eicosane ($C_{20}H_{44}$) and tetracosane ($C_{24}H_{50}$). Examples of products that fall in this range are heavy fuel oils, lubricating oils, and waxes[9-11].

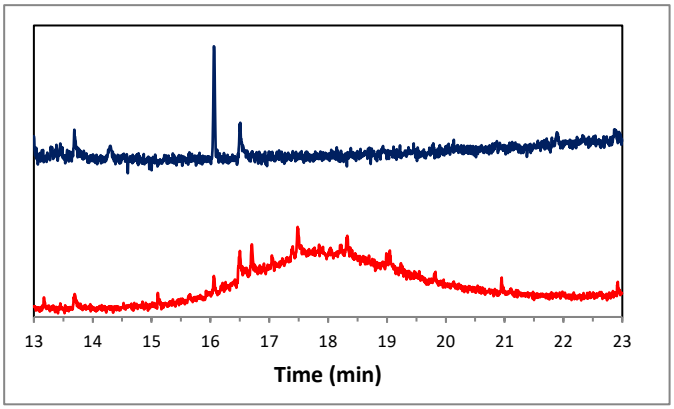


Figure 4: Comparison of C25 reference fuel (top) and a car fuel sample (bottom) exhibiting peaks for straight and branched alkanes (C_{20} – C_{24}). See Materials and methods section for instrument parameters.

The second VP fuel, C23, had similar components, with the addition of toluene. An example chromatogram is shown in Figure 5.

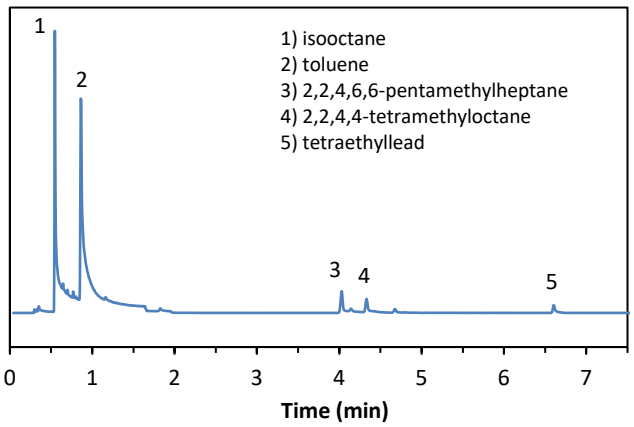
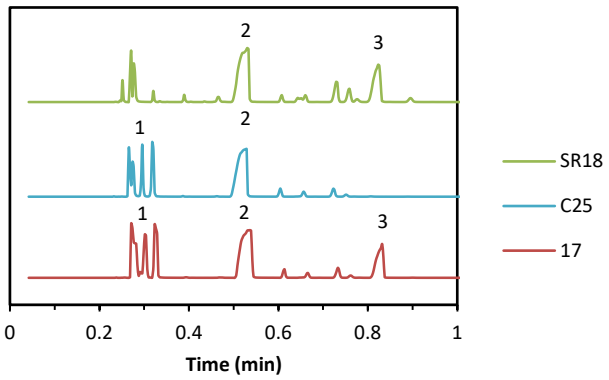


Figure 5: Example chromatogram of VP C23 fuel. See materials and methods section for instrument parameters.



Peaks: 1) 2,2-dimethylbutane, 2) isooctane, 3) toluene

Figure 6: Expanded view of the first minute from chromatograms of two reference racing gasolines (SR18 and C25) and fuel from a vehicle fuel tank (17). See materials and methods section for instrument parameters.

In 2015, the NHRA switched fuel suppliers from VP to Sunoco. VP C25 has three components (2,2-dimethylbutane, 2,2,4,4-tetramethyloctane, and 2,2,7,7-tetramethyloctane) that are not present in Sunoco SR18. Furthermore, Sunoco SR18 racing gasoline contains toluene. During the transition period, the fuels from racing teams were monitored to ensure that all teams were being compliant and using the new standard fuel.

A questioned fuel was analysed along with standards of known SR18 and VP C25 fuels. Preliminary analysis consisted of specific gravity measurements, where specific gravity at a given temperature is the ratio of the density of a substance to the density of a reference, in this case HPLC water. Specific gravity is used as a tool in fuel monitoring since it can be an indicator of chemical composition. The reported value for Sunoco SR18 was 0.70. The experimentally determined specific gravity values for the two reference fuels and the unknown fuel were very similar, ranging from 0.697 to 0.709 with precisions of 0.2% - 0.5% (RSD). Acceptable limits have not yet been set by the NHRA and additional testing is required to determine at what concentration adulteration can be detected using this technique. The questioned fuel had an experimentally determined specific gravity of 0.701. Therefore, the specific gravity test was not sufficiently sensitive to detect if the fuel was mixed.

Hence, a confirmatory TV-SPME/GC/MS analysis was required. The compounds eluting within the first minute of the chromatograms for the reference and unknown fuels are shown in Figure 6. A peak from 2,2-dimethylbutane is found in C25 but not SR18. This peak is also present in the questioned car sample (indicated with an arrow in the chromatogram for car 17). Both isomers of tetramethyloctane (2,2,4,4-tetramethyloctane and 2,2,7,7-tetramethyloctane) are also found in C25 fuel and they were also present in the car sample (data not shown). It was ultimately concluded that the fuel was illegally adulterated.

Conclusions

Two GC/MS methods based upon total vaporization of the sample have been developed to identify compounds in racing fuels. These results provide a comprehensive picture of normal/abnormal fuel compositions. All methods have been validated for the application to NHRA related standards and samples and these methods and protocols will be used for future quality control testing.

Acknowledgements

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References

1. E. Lotspeich, K. Kitts and J. Goodpaster, *Forensic Sci. Int.*, 2012, 220, 130-134.
2. K. U. Alwis, B. C. Blount, L. K. Silva, M. M. Smith and K.-H. Loose, *Environmental science & technology*, 2008, 42, 2522-2527.
3. A. Takeuchi, Y. Nishimura, Y. Kaifuku, T. Imanaka, S. Natsumeda, H. Ota, S. Yamada, I. Kurotani, K. Sumino and S. Kanno, *Journal of occupational health*, 2010, 52, 194-197.
4. L. Moreira, L. d'Avila and D. Azevedo, *Chromatographia*, 2003, 58, 501-505.
5. R. M. Balabin, R. Z. Safieva and E. I. Lomakina, *Analytica Chimica Acta*, 2010, 671, 27-35.
6. L. Zoccolillo, M. Alessandrelli and M. Felli, *Chromatographia*, 2001, 54, 659-663.
7. C. L. Rainey, D. E. Bors and J. V. Goodpaster, *Analytical Chemistry*, 2014, 86, 11319-11325.
8. D. Bors and J. Goodpaster, *Anal. Methods*, 2015, 7, 9756-9762.
9. R. O. Keto, *Journal of Forensic Sciences*, 1995, 40, 412-423.
10. J. Lentini, J. Dolan and C. Cherry, *Journal of Forensic Science*, 2000, 45, 968-989.

11. H. Lai, A. Leung, M. Magee and J. Almirall, *Analytical and Bioanalytical Chemistry*, 2010, 396, 2997-3007.